Accelerated Testing Validation

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> Project ID # FC016

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Project Overview

Timeline

- Project Start Date
 - August 2009
- Project Duration
 - 4 Years (1 year extension)
- Project End Date
 - Sept. 2014

Budget

- Total project funding
 - 5 Years : \$4,409,790
 - DOE Cost : \$4,350,000
 - Cost Share : \$159,790
- Funding for FY13/FY14 LANL Partners (Industry) Other National Labs FY13/FY14 Total
 - \$ 750k, 350k \$ 98k, <u>\$ 172k, 150k</u> \$1020k, 500k

Barriers

- Fuel cells: 2011 Technical Plan
- A. Durability
 - Automotive Target
 - 5,000 hours (10% degradation)
 - Stationary Targets
 - 2017 : 40,000 hours (20% degradation) 2020 : 60,000 hours (20% degradation)

Bus Target

2016 : 18,000 hours

Accelerated testing protocols need to be developed to enable projection of durability and to allow for timely iterations and improvements in the technology.

Partners

- Ballard Power (System Integrator)
- Ion Power (Materials Supplier)
- ORNL (Metal Bipolar Plates)
- LBNL (Modeling)

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Objectives/Barriers - Relevance

The objectives of this project are 3-fold

- 1. Correlation of the component lifetimes measured in an AST to real-world behavior of that component.
- 2. Validation of existing ASTs for Catalyst layers and Membranes
- 3. Development of new ASTs for GDLs, bipolar plates and interfaces

Technical Targets

Automotive : Durability with cycling: 5,000 hours (2010/2015): 2005 Status (2000 hours for stack and 1000 hours for system) Stationary : Durability: 40,000 hours (2011): 2005 Status = 20,000 hours Bus Data : 18,000 hours (2016); 25,000 hours (ultimate); Status = 12,000 hours.

Importance of Accelerated Stress Test (AST)

- Allows faster evaluation of new materials and provides a standardized test to benchmark existing materials
- Accelerates development to meet cost and durability targets
- Different ASTs are available (DOE-FCTT, USFCC and JARI)
 - Lack of correlation to "Real World" Data
 - No tests available for GDLs and other cell components
 - Value of combined vs individual tests

BALLARD

Approach





Approach - Milestones

1	Q1	12/31/2013	Complete comparison of DOE FCTT ASTs for carbon corrosion (1.2V hold and 1.0 to 1.5V cycles) and record the differences	Complete (≈ 100 times faster decay rates)
2	Q2	3/31/2014	Demonstrate GDL AST results that have comparable GDL degradation as those observed in an approximately 1000 hour fuel cell drive cycle test	Complete (Performance is MEA dependant)
3	Q3	6/30/2014	Propose AST for membrane degradation and quantify acceleration factor with respect to drive-cycle data. Verify that AST has at least an acceleration factor of 10	On track
4	Q4	9/30/2014	Propose AST for catalyst degradation and quantify acceleration factor with respect to drive-cycle data. Verify that AST has at least an acceleration factor of 10	

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- GoreTM MEAs
 - Gore[™] Primea[®] MESGA MEA A510.1/M720.18/C510.2
 - Gore[™] Primea[®] MESGA MEA A510.2/M720.18/C510.4
 - Gore[™] Primea[®] MESGA MEA A510.1/M710.18/C510.2
- Ballard P5 and HD6 MEAs
- Ion Power MEAs
 - DuPont[™] XL membranes
 - Tanaka Catalysts
 - TEC10E50E, TEC10E40E, TEC10E20E, TEC10E10E, TEC10E05E (High Surface area carbon 50 wt%, 40 wt% and 20 wt% Pt)
 - TEC10V40E, TEC10V20E, TEC10V10E, TEC10V05E (Vulcan carbon 40 wt%, 20 wt%, 10 wt%, and 5 wt% Pt)
 - TEC10EA40E, TEC10EA20E, TEC10EA10E, TEC10EA05E (Low Surface area carbon 40 wt%, 20% wt%, 10 wt%, and 5 wt% Pt)
- GDL
 - SGL SIGRACET[®] 24BC (5% PTFE-substrate/23% PTFE MPL; 84% substrate porosity)
 - SGL SIGRACET[®] 25BC (5% PTFE-substrate/23% PTFE MPL; 88% substrate porosity)
 - Varying PTFE content and substrate porosity

M710 : Discontinued product. Lower chemical and mechanical durability sample

M720 : technology circa 2005. Higher chemical and mechanical durability sample



Correlation of AST, Field Data and Drive Cycle

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Start/stops is the primary correlation to performance decay. Consistent with low number of > 100 mV transients

System	P5 (1)	P5 (2)	P5 (3)	HD6
Hours of operation	2769	3360	2597	6842
Degradation rate (BOL to EOL) @ ≈ 0.5 A/cm2 (μV/cell/hr)	31.4	33.5	26.3	5.2
≈ Transients ≥ 100 mV	225	270	350	1100
Total # of Air/Air Starts	361	417	263	< 100
Voltage (%cycle > 0.8V/cell)	52	48	53	57

> 30,000 cycles ≈ 133 hours.

Try modified FCCJ protocol instead of DOE's triangular wave

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- 30,000 cycles ≈ 2000 hours of bus operation (Both P5 and HD6)
- 30,000 cycles ≈
 850 hours of US
 DRIVE Drive Cycle
- 30,000 cycles ≈
 500 hours of wet drive cycle
- 5000 hours ≈ 175,000 cycles
- Need >> 30,000 cycles for 5000 hour automotive durability

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New FCTT AST (1 to 1.5V cycle) : Performance

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New FCTT AST (1 to 1.5V cycle) : Diagnostics

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Compare New and Old AST: Amount of C Corroded /Progress



Approximately 1 order of magnitude greater carbon corrosion rate
 Correlates to decrease in catalyst layer thickness and increased catalyst layer compaction associated with increased mass transport resistance

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Compare new and old AST : Catalyst Sintering

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Support AST



- ➤ ≈ 150 times faster decay in fuel cell performance
- > \approx 100 times faster Pt growth rate during cycling
- Faster decay rate initially and tapering later as you corrode more carbon and stabilize the Pt particle size at around 5 nm

Accomplishments /Progress

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Compare new and old AST : Performance

/Prog



Support AST

- ➤ ≈ 150 times faster decay in fuel cell performance on multiple carbon types
- ➤ ECSA and Mass activity decay also enhanced by ≈ 150 times
- ➢ New AST is faster and retains the same degradation mechanism. Should also correspond to # of worst case scenario unmitigated start/stops

Membrane Degradation : Damage Mechanisms

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Membrane AST

HD6 Field Sample

a) membrane cracking

P5 Field Sample



P5 sample after H₂/Air RH cycling AST



b) membrane thinning



 Membrane global thinning due to chemical degradation (accelerated by OCV under dry conditions)
 Membrane cracking and local thinning due to mechanical stresses (accelerated by RH cycling)
 Field sample can be replicated only by combined

mechanical/chemical degradation

Membrane Degradation : FCTT Drive Cycle

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- Membranes without chemical and mechanical stabilization fail early in the drive cycle tests (< 500 hours) and fail even under wet only testing (< 1000 hours)</p>
- ➤ Membranes with chemical and mechanical stabilization (DuPontTM XL) last > 2500 hours
 - $\checkmark\,$ One sample failed at 2300 hours due to test stand failure
 - ✓ The DuPont[™] XL membrane failed at the edges due to absence of sub gasket
 - ✓ After 3800 hours: ≈ 30% thinning (mainly on cathode side of support)

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Current Membrane ASTs : Damage Mechanisms

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Membrane AST DuPont[™] XL 307 hours @ OCV





DuPont[™] XL 20098 RH Cycles

- Chemical Degradation (OCV @ 90 °C, 30% RH)
 - $\checkmark\,$ Cathode side of membrane is completely missing after 307 hours of OCV
 - ✓ More severe compared to drive cycle and field data
- Mechanical Degradation (RH cycling @ 80 °C in Air)
 - ✓ No visible degradation after 20,000 RH cycles
 - $\checkmark\,$ Most supported membranes are untouched by this AST

Proposed Membrane AST : Damage Mechanism

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DuPont[™] XL 9934 Cycles Membrane AST







> RH Cycling in H_2 /Air. Cell = 90 °C, Humidifier bottles = 92 °C (2 mins dry and 2 mins wet)

- Pt band in membrane observed
- Lateral cracks observed
- Membrane cracking observed
- Membrane thinning observed only in un-stabilized membranes

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Proposed Membrane AST : Modeling

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Membrane AST

100000



- SAXS: Field data similar to H₂/Air RH cycling AST
- Stress assisted void growth model developed at LBNL showing relevance of combined chemical/mechanical AST
- Temperature can be used as an accelerating factor

rrrr

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RH cycling

Proposed Membrane AST : Operating Conditions

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Membrane AST



- RH cycling under OCV @ 80 °C: Stabilized membranes last > 55 days (20,000 cycles)
- RH cycling under OCV @ 90 °C: Thinning of N211 observed but still no thinning of DuPontTM XL. Need to accelerate chemical degradation with respect to mechanical
- > Increase time of dry cycle with respect to wet cycle keeping total cycle time constant

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GDL Degradation : Reported Work

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GDL AST





Figure 4. Cell performance measured at 1 A/cm^2 after exposure of 3-cell stack to air/air cycles (Table I protocol). Cell 3 is identical to cell described in Fig. 2. Cells # 1 and 2 are identical to cell # 3, except for the cathode GDLs, which is described in Table II.

M. L. Perry et al, ECS Transactions, 33(1), 1081 (2010)

- GDL degradation is prominent at low Pt loadings, very thin/very thick catalyst layers and under wet/cool conditions
- UTRC has published data showing MPL degradation is an issue during Air/Air holds
- GDL AST reported by Decode project, Peter Wilde: SGL Carbon
 - Boil in 30%H₂O₂ @ 95 °C

same cell shown in Fig. 2.

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Previously Reported GDL AST

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➢ Boil in 30%H₂O₂ @ 95 °C

- Aged GDLs show loss in hydrophobicity (decrease in contact angle)
- Aged GDLs show decreased porosity in the MPL
- GDLs aged in peroxide show increased mass transport resistance in fuel cell applications

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GDL Degradation : In Situ vs Ex Situ

GDL AST

Accomplishments

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Figure 8.10. Comparison of RH-sensitivity scans for cells built with fresh SGL GDL 24BC (cell M5) and GDL 24BC aged in LAES chamber for 1006 hr (cell M2). Aging conditions were 80°C DI water and an air sparging gas; see Figure A.11 in Appendix A for cell M2 lifetesting data.

David L. Wood III; Ph.D Thesis, UNM (2007)

- Ex situ ageing effects similar to in situ fuel cell ageing
- Lower HFR and better performance at low RH
- Decreased performance at high RH



/Progress

GDL AST : Operating Conditions



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- Slower degradation observed after 80 °C ageing
- Initial tests indicate similar degradation rates in ex situ and in situ aged GDLs
- Further testing in progress using low loaded MEAs

Responses to Previous Year Reviewers' Comments

- Carbon corrosion at low potentials is reported to be significant @ 0.9 V; did the researchers quantify the value? Is there a dependence on the type or manufacturer of the carbon? Again, the information is somewhat elusive.
 - Carbon corrosion results have been presented in detail on three different carbons. The high surface area carbons have significant corrosion rates at those low potentials. These results have been published in ECS Transactions, 50 (2) 1589-1597 (2012).
- How does LBNL confirm the "collapse of cathode structure"? Is the collapse gradual or occurs at some catastrophic condition. Again, more information should be given.
 - The collapse of the catalyst layer is confirmed by TEM analysis at ORNL. LBNL utilizes this information in the VLB modeling. The loss is gradual (see slide from ORNL in reviewer only section).
- For the voltage loss breakdown analysis; what does simultaneous fitting of air and HelOx data at different current densities mean? Was the work done or is this a statement of future activity?
 - The fitting of data in air and HelOx simultaneously means that only the gas diffusion of O₂ is different and all other parameters are kept constant in fitting the polarization curve. This is done. A more robust fit would be the simulation the entire impedance spectrum and this is in the future work.
- The AST related to GDL ageing is not relevant for field failure.
 - We believe that these ASTs will be relevant when low loaded MEAs are used in the field.
- Study the impact of these ASTs on the state of the art MEAs.
 - Currently utilizing chemically and mechanically stabilized membranes and graphitized carbons. Will expand to include alloy work. Exploring possibility of using MEAs from GM.



Collaborations

LANL (Rangachary Mukundan, Rodney Borup, John Davey, David Langlois, Dennis Torraco, Karen Rau, Roger Lujan, Dusan Spernjak, Joe Fairweather and Fernando Garzon)

• Co-ordinate project; Perform all ASTs and Drive cycle testing; Materials Analysis of BOL and EOL materials

Ballard Power Systems (Paul Beattie)Analyze Bus voltage cycling and RH cycling data

LBNL (Adam Weber)

Detailed Voltage loss break-down and full AC impedance modeling

Ion Power (Steve Grot) Deliver custom MEAs with varying durability ORNL (Karren More) TEM

W. L. Gore and Associates Inc., and SGL Carbon (materials suppliers)

Durability working group (Start/Stop protocol)

Future Work

- Evaluate modified FCCJ's catalyst cycling AST
 - Trapezoid wave with 0.5s rise time from 0.6V to 0.95V, 2.5s hold at 0.95V, 0.5s from 0.95 to 0.6V, and 2.5s hold at 0.6V @ 80 °C, 100% RH, H_2/N_2
- Expand into MEAs based on Pt-Ni alloy catalysts and low (Pt < 0.1 mg.Pt/cm²)
- Perform DWG start/stop protocol on three different carbon based MEAs
- Evaluate catalyst layer AST including OCV testing and catalyst layer performance (0.6 to 1.2V cycle in H₂/Air)
- Evaluate RH cycling in H₂/Air using 1 min or 30 sec wet cycle time and 3 mins or 3.5 mins dry cycle time
- Continue long term drive cycle testing to evaluate effectiveness of membrane AST
- Model combined Mech/Chem degradation AST to try to accelerate it further
- Model voltage loss breakdown : include full impedance spectra

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Summary

- New Carbon Corrosion AST
 - 1 to 1.5V cycling corrodes carbon 10X faster than 1.2V hold
 - 1 to 1.5V cycling results in ≈ 100X faster voltage, ECSA and MA decay and Pt particle size growth (Similar degradation mechanisms)
- Membrane AST
 - OCV too severe and RH cycling too benign to predict membrane lifetimes
 - RH cycling under OCV qualitatively similar to field and drive cycle data
 - RH cycling under OCV @ 80°C too benign (tests longer than 55 days, 20,0000 cycles for stabilized membranes)
 - RH cycling under OCV @ 90°C is faster but still needs acceleration of chemical degradation with respect to mechanical degradation (longer dry cycles)
- GDL AST
 - GDL AST results in similar degradation to that observed in drive cycle testing and in situ fuel cell testing
 - Quantification requires further testing

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Fuel Cell Tech Team (Craig Gittleman, Jim Waldecker and Balsu Lakshmanan) for guidance on ASTs

W. L. Gore and Associates (MEAs)

SGL Carbon (GDLs)

Technical Backup Slides



Tech Team Protocol (Pt Catalyst)

Table 1 Electrocatalyst Cycle and Metrics Table revised March 2, 2010				
Cycle	Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V. Single cell 25-			
	50 cm^2			
Number	30,000 cycles			
Cycle time	16 s			
Temperature	80°C			
Relative Humidity	Relative Humidity Anode/Cathode 100/100%			
Fuel/Oxidant	ant Hydrogen/N ₂ (H ₂ at 200 sccm and N ₂ at 75 sccm for a 50 cm ² cell			
Pressure Atmospheric pressure				
Metric	Frequency	Target		
Catalytic Mass	At Beginning and End of Test	\leq 40% loss of initial catalytic		
Activity*	minimum	activity		
Polarization curve	After 0, 1k, 5k, 10k, and 30k cycles	\leq 30 mV loss at 0.8 A/cm ²		
from 0 to ≥1.5 A/cm ^{2**}				
ECSA/Cyclic	After 10, 100, 1k, 3k, 10k, 20k and	$\leq 40\%$ loss of initial area		
Voltammetry***	30k cycles			

* Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H₂ (bal N₂)/O₂ {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.

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** Polarization curve per Fuel Cell Tech Team Polarization Protocol in Table 5.

*** Sweep from 0.05 to 0.6V at 20mV/s, 80°C, 100% RH.

Tech Team Protocol (Catalyst Support)

Table 2				
Table 2 Catalyst Support Cycle and Metrics Table revised March 2, 2010				
Cycle	Hold at 1.2 V for 24 h; run polarization curve and ECSA; repeat for total 400 h. Single cell 25-50 cm ²			
Total time	Continuous operation for 400 h			
Diagnostic frequency	24 h			
Temperature	80°C			
Relative Humidity	Anode/Cathode 100/100%			
Fuel/Oxidant	Hydrogen/Nitrogen			
Pressure	150 kPa absolute			
Metric	Frequency	Target		
Catalytic Activity*	Every 24 h	\leq 40% loss of initial catalytic		
		activity		
Polarization curve from	Every 24 h	\leq 30 mV loss at 1.5 A/cm ² or rated		
0 to \geq 1.5 A/cm ^{2**}		power		
ECSA/Cyclic Voltammetry***	Every 24 h	$\leq 40\%$ loss of initial area		

* Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% H₂ (bal N₂)/O₂ {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.

** Polarization curve per Fuel Cell Tech Team Polarization Protocol in Table 5

*** Sweep from 0.05 to 0.6V at 20mV/s, 80°C, 100% RH. Old AST

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Tech Team Protocol (Catalyst Support)

Table A-2. Catalyst Support Cycle and Metrics			
	Table revised January 14, 2013		
Cycle	Triangle sweep cycle: 500 mV/s between 1.0 V and 1.5 V; run polarization curve and ECSA; repeat for total 400 h. Single cell 25–50 cm ²		
Number	5000 cycles		
Cycle time	2 seconds		
Temperature	80°C		
Relative humidity	Anode/cathode 100/100%		
Fuel/oxidant Hydrogen/nitrogen			
Pressure	Atmospheric		
Metric	Frequency	Target	
Catalytic activity*	At beginning and end of test, minimum	<u><</u> 40% loss of initial catalytic activity	
Polarization curve from 0 to ≥1.5 A/cm ^{2**}	After 0, 10, 100, 200, 500, 1k, 2k, and 5k cycles	<30 mV loss at 1.5 A/cm ² or rated power	
ECSA/cyclic voltammetry***	After 0, 10, 100, 200, 500, 1k, 2k, and 5k cycles	≤40% loss of initial area	

* Mass activity in A/mg @ 150 kPa abs, backpressure at 857 mV iR-corrected on 6% H₂ (bal N₂)/O₂ {or equivalent thermodynamic potential}, 100% RH, 80°C normalized to initial mass of catalyst and measured before and after test.

** Polarization curve per Fuel Cell Tech Team Polarization Protocol in Table A-5.

*** Sweep from 0.05 to 0.6 V at 20 mV/s, 80°C, and 100% RH.

New AST

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Tech Team Protocol (Membrane/Chemical)

Table 3 MEA Chemical Stability and Metrics Table revised December 10, 2009				
Test ConditionSteady state OCV, single cell 25-50 cm²				
Total time	500 h			
Temperature	90°C			
Relative HumidityAnode/Cathode 30/30%		_		
Fuel/Oxidant	Hydrogen/Air at stoics of 10/10 at 0.2 A/cm ² equivalent flow			
Pressure, inlet kPa abs (bara) Anode 150 (1.5), Cathode 150 (1.5)				
Metric	Frequency	Target		
F release or equivalent for	At least every 24 h	No target – for monitoring		
non-fluorine membranes				
Hydrogen Crossover	Every 24 h	$\leq 2 \text{ mA/cm}^2$		
$(mA/cm^2)*$				
OCV	Continuous	$\leq 20\%$ loss in OCV		
High-frequency resistance	Every 24 h at 0.2 A/cm^2	No target – for monitoring		
Shorting resistance**	Every 24 h	>1,000 ohm cm ²		

* Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical hydrogen crossover method.

** Measured at 0.5V applied potential, 80°C and 100% RH N_2/N_2 . Compression to 20% strain on the GDL.



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Tech Team Protocol (Membrane/Mechanical)

Table 4 Membrane Mechanical Cycle and Metrics (Test using a MEA) Table revised December 10, 2009			
Cycle	Sycle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25-50		
	cm ⁻		
Total time	Until crossover >2 mA/cm ² or 20,000 cycles		
Temperature	'emperature 80°C		
Relative Humidity	Cycle from 0% RH (2 min) to 90°C dewpoint (2 min)		
Fuel/Oxidant	Air/Air at 2 SLPM on both sides		
Pressure	Ambient or no back-pressure		
Metric	Frequency	Target	
Crossover*	Every 24 h	$\leq 2 \text{ mA/cm}^2$	
Shorting resistance**	Every 24 h	$>1,000 \text{ ohm cm}^2$	
* Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical			

hydrogen crossover method.

** Measured at 0.5 V applied potential, 80°C and 100% RH N_2/N_2 . Compression to 20% strain on the GDL.



Drive Cycle Testing

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Use 100% H_2 instead of 80% H_2

Only one station capable of RH control (bottle = 90°C, adjust dry and wet flows) Also performing cycles at the high RH conditions (Wet Cycling)